GEOPHYSICAL RESEARCH LETTERS, VOL. 25, NO. 6, PAGES 907-910, MARCH 15, 1998

A global modeling study of solid rocket aluminum oxide emission effects on stratospheric ozone

Charles H. Jackman, [1] David B. Considine, [2,1] and Eric L. Fleming [3,1]

Abstract. Recent laboratory measurements [Molina et al. 1997] have indicated that the heterogeneous chlorine activation reaction $ClONO_2 + HCl \longrightarrow HNO_3 + Cl_2$ has a reaction probability of about 0.02 on aluminum oxide particles (alumina). Since alumina is among those substances emitted by solid rocket motors (SRMs), we have assessed the heterogeneous chemical impact of SRM-emitted alumina on stratospheric ozone using the Goddard Space Flight Center two-dimensional photochemistry and transport model. Historical launch rates of the Space Shuttle, Titan III, and Titan IV rockets were used in time-dependent and steady-state model calculations. Variations in the temporal ozone decreases reflected the fluctuation in launch rate frequency. The annually averaged global total ozone (AAGTO) is computed to decrease by 0.025% by the year 1997. About one-third of this AAGTO change results from the SRM-emitted alumina while about two-thirds is due to SRM-emitted hydrogen chloride.

1. Introduction

The launch of solid rocket motors (SRMs) injects aluminum oxide particles (alumina), hydrogen chloride, carbon monoxide, water vapor, and molecular nitrogen directly into the stratosphere. Local effects on Cl_2 and ozone due to SRMs have recently been measured by Ross et al. [1997a,b]. We focus on the global effects of SRMs in this modeling study.

The global effects of the chlorine compounds emitted by the SRMs of the Space Shuttle and Titan IV launch vehicles on the stratospheric ozone layer have been studied previously using a purely gas phase atmospheric chemical scheme [Prather et al. 1990] and including heterogeneous reactions on background stratospheric sulfate aerosol particles and polar stratospheric clouds [Jackman et al. 1996a]. Recently, Molina et al. [1997] showed that alumina particles promote the chlorine activation reaction $ClONO_2 + HCl \longrightarrow HNO_3 + Cl_2$ with a reaction probability of about 0.02 on the particle surfaces. If alumina particles become coated by H_2SO_4 in the atmosphere they would result in a small increase in the background sulfate particle burden, a minor effect. However, if they remain uncoated, the alumina particles would have a higher potential for ozone depletion because the rate of the above-mentioned chlorine activation reaction is faster on alumina than sulfate particles at most stratospheric temperatures. Molina et al. [1997] argue that the alumina particles will probably remain uncoated throughout most of their stratospheric residence time and hence promote chlorine activation.

Several previous studies have considered the issue of heterogeneous processes on the SRM-emitted alumina. For example, Danilin [1993] and Denison et al. [1994] found that ozone in or near the plume was affected in only a minor way when heterogeneous reactions on alumina were included. Jones et al. [1995] studied the global impact on ozone from an Ariane 5 launch rate of ten per year with the use of a two-dimensional model. They assumed that the alumina would become coated by H_2SO_4 and calculated about a 1% increase in the aerosol layer due to the alumina.

Since the alumina particles are present at all latitudes in all seasons, rather than concentrated in the polar winter like the polar stratospheric clouds, and the reaction probability for chlorine activation is not temperature sensitive, alumina particles offer the potential to impact ozone if they remain uncoated by H_2SO_4. We use the Goddard Space Flight Center (GSFC) two-dimensional photochemistry and transport model to evaluate the impact of SRM-emitted alumina on stratospheric ozone.

2. Treatment of Aluminum Oxide

There have been a few measurements of alumina emissions from SRMs over the past 20 years. Strand et al. [1981] measured submicron alumina particle size distributions in a Space Shuttle SRM plume. Cofer et al. [1987, 1991] added plume measurements to determine the alumina size distributions in the 0.3 to 10 micron range. These measurements were combined by Brady and Martin [1995] into a single trimodal size distribution describing alumina particles in the SRM plume. The three modes corresponded to small, medium, and large particles and each were represented as exponentials:

$$N_i(r) = A_i exp(-r/r_i) \quad (1)$$

where $N_i(r)dr$ gives the number of particles in the mode per cubic meter of air having a radius between r and $r + dr$, A_i is an exponential prefactor, and r_i is the

[1] Code 916, NASA Goddard Space Flight Center, Greenbelt, MD 20771, (e-mail: jackman@assess.gsfc.nasa.gov)

[2] Joint Center for Earth System Science, University of Maryland, College Park, MD

[3] Space Applications Corporation, Vienna, VA

Paper number 98GL00403.
0094-8534/98/98GL-00403$05.00

mean radius of the particle mode. Brady and Martin [1995] supply values for both r_i and A_i. These values indicate that 0.12, 0.08, and 0.80 fraction of the mass enters the small, medium, and large particle modes, respectively. The mode mean radii are given as 0.012, 0.14, and 0.56 microns, respectively.

In this work we use a particle size distribution similar to that of Brady and Martin [1995]:

$$N(r) = \sum_{i=1}^{3} B_i exp(-r/r_i) \quad (2)$$

Here, we assume that the mode mean radii are constant in time and the same as in Brady and Martin. The values for the exponential prefactors vary in time and space depending on the emission rate of the SRM exhaust and the manner in which alumina is transported through the model atmosphere. We assume that the mass emitted into each particle mode is consistent with the Brady and Martin values. The emitted alumina particles are then subject to model transport processes as well as gravitational settling. A simple calculation assuming the Stoke's r^2 relationship between particle size and fall speed [e.g., Rogers, 1979] shows that the sedimentation mass flux of particulate alumina distributed according to (2) is proportional to the settling rate of the mode mean radii. To calculate the settling rate, we use the formula of Kasten [1968].

3. Steady-State Model Simulations and Results

All simulations were completed with the latest version of the GSFC 2D photochemical and transport model described in Jackman et al. [1996b]. We computed several model simulations and investigated the sensitivity of the model results to various assumptions about the alumina particles and their effects. A brief description of each model simulation is given in Table 1. The base simulation "A" contained no Space Shuttle or Titan IV launches. All other simulations included a launch rate of nine Space Shuttle and three Titan IV rockets per year as in Jackman et al. [1996a]. The HCl stratospheric emissions for this launch scenario are as given in Jackman et al. [1996a, Table 1].

Other model results have predicted [e.g., Denison et al. 1994] that HCl could be converted to Cl_2 in afterburning reactions in the exhaust plume. Ross et al. [1997a] recently confirmed these predictions by measuring Cl_2 in a Titan IV exhaust plume. The form of chlorine injected into the stratosphere will make a difference for computations of ozone loss in the plume on short time scales [e.g., Danilin, 1993]. However, Jones et al. [1995] show that the form of chlorine emitted by the Ariane 5, another solid rocket motor, makes very little difference in global ozone loss computations for time periods over a few weeks after launch. Since our model computations are meant to simulate the long-term effects (time-scales greater than a few weeks) from rocket launches, the form of SRM-emitted chlorine is not an issue, and we assume it is all emitted as HCl.

The stratospheric emissions of Al_2O_3 from one Space Shuttle and one Titan IV rocket launch are 112 and 69 tons, respectively [see Brady et al. 1994]. These Al_2O_3 emissions can be compared to the HCl stratospheric emissions by one Space Shuttle and one Titan IV rocket launch of 68 and 38 tons, respectively [as used in Prather et al. 1990 and Jackman et al. 1996a]. The altitude distribution of the Al_2O_3 emissions from the two vehicles is similar to that given for the HCl emissions in Jackman et al. [1996a, Table 1].

The steady-state model simulations were run for twenty model years to a seasonally repeating condition. The ground boundary conditions of the long-lived source gases for steady-state 1990 conditions are taken from Jackman et al. [1996a, Table 2]. The reaction $ClONO_2 + HCl \longrightarrow HNO_3 + Cl_2$ with a reaction probability of 0.02 [following Molina et al. 1997] was included on alumina particles in scenarios "C", "D", "E", and "F".

The predicted annually averaged global total ozone (AAGTO) percentage change for the various steady-state simulations are given in Table 1. Scenario "B", which includes SRM HCl emissions only, is the same as our Jackman et al. [1996a] simulation which included gas phase reactions and heterogeneous reactions

Table 1. Description of steady-state model simulations and annually-averaged global total ozone (AAGTO) percentage change relative to simulation "A". The designation "EMF" or "Emitted Mass Fractionation" with the three fractions following refer to the amount of alumina mass assumed to be emitted in each of the three particle size distributions.

Simulation	Description	% AAGTO Change
A	Base (no rocket launches)	—
B	HCl emission only	$-2.3\text{x}10^{-2}$
C	Al_2O_3 emission only - EMF: (1) 0.12, (2) 0.08, and (3) 0.80	$-1.0\text{x}10^{-2}$
D	HCl (as in B) and Al_2O_3 emissions (as in C)	$-3.3\text{x}10^{-2}$
E	Al_2O_3 emission only - EMF: (1) 0.0, (2) 0.0, and (3) 1.0	$-5.2\text{x}10^{-5}$
F	Al_2O_3 emission only - EMF: (1) 1.0, (2) 0.0, and (3) 0.0	$-8.5\text{x}10^{-2}$
G	Al_2O_3 emission only - EMF: (1) 0.12, (2) 0.08, and (3) 0.80 ONLY added to sulfate aerosol distribution	$-3.1\text{x}10^{-3}$
H	Al_2O_3 emission only - EMF: (1) 0.12, (2) 0.08, and (3) 0.80 ONLY decomposition of CF_2Cl_2 with γ=$2\text{x}10^{-5}$	$+4.2\text{x}10^{-5}$

on the stratospheric sulfate aerosol layer and polar stratospheric clouds. The GSFC model has been improved over the past two years resulting in a moderately different AAGTO percentage change. Present computations give a decrease of 0.023% whereas Jackman et al. [1996a] calculated a decrease of 0.014%. This difference between the two versions of the GSFC model give an indication of the uncertainty in these simulations.

Scenarios "C" and "F" show AAGTO decreases (relative to "A") competitive with or larger than that computed for scenario "B" [0.010% and 0.085% versus 0.023%]. These scenarios include a mass fraction of emitted alumina particles in the smallest size distribution of 0.12 ("C") and 1.00 ("F"). We calculated the yearly average surface area for scenario "C" of the Al_2O_3 particles. The smallest particles contribute more than 95% of the calculated alumina surface area in the stratosphere. The largest particles with mean radius r_3 = 0.56 microns fall out of the stratosphere fairly rapidly with most of the mass being removed within weeks and contribute only a few percent to the stratospheric alumina surface area. The medium particles are even less important than the large particles and contribute only a couple percent to the stratospheric alumina surface area due to the small emission of exhaust into this mode. The maximum alumina surface area in case "C" is calculated to be 2.5×10^{-3} $\mu m^2/cm^3$ in the lower stratosphere middle to polar northern latitudes. For comparison, a typical value for the background sulfate surface area density is 1 $\mu m^2/cm^3$.

Maximum changes in total ozone are computed in the northern and southern polar regions throughout the winter and early spring for scenario "B" (HCl emissions only), whereas maximum changes in total ozone are computed in the spring for scenario "C" (Al_2O_3 emissions only). Simulation "D", which includes both the HCl emissions (as in "B") and the Al_2O_3 emissions (as in "C"), is our most reasonable simulation of the effects of SRMs on the stratosphere and is shown in Figure 1. The AAGTO decrease for "D" relative to "A" is 0.033%. The effect on ozone from the emissions of HCl and Al_2O_3 add approximately linearly on a global basis. The largest total ozone decreases are predicted to be about 0.12% at polar latitudes in the spring of both hemispheres.

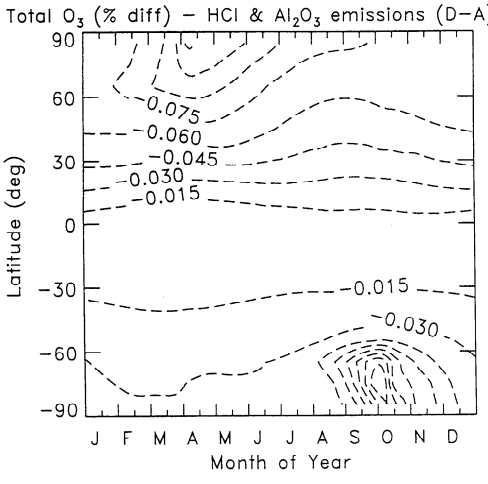

Figure 1. GSFC model calculated total ozone change (percent) for latitude by month of year comparing simulations "D" to "A". Simulation "D" assumes a steady-state launch rate of nine Space Shuttles and three Titan IV vehicles per year.

If it is assumed that all of the emitted alumina particles are in the large size distribution (scenario "E"), the AAGTO computed decrease is an extremely small 5.2×10^{-5}%. If we increase the emission of alumina in the smallest sized particles by a factor of 8.3 for scenario "F", this results in an increase in the maximum calculated alumina surface area by a factor of 8.3. We also compute a nearly linear increase in ozone loss to 0.085% for scenario "F" when compared to the 0.01% in scenario "C". Scenario "F", which assumes all of the alumina particles are in the small size distribution, is an upper limit computation within the assumptions going into our trimodal size distribution. There is no reason to believe that all the particles are in the smallest size distribution, since the alumina particles do coalesce and there are very good measurements of large particles in SRM exhaust plumes [Cofer et al. 1987, 1991].

If it is assumed that the alumina particles are rapidly coated with H_2SO_4 and add only to the sulfate surface area (scenario "G"), the AAGTO computed decrease is 3.1×10^{-3}%, over a factor of three smaller than that computed in scenario "C". A coating of H_2SO_4 changes the heterogeneous chemistry occurring on the alumina particle and dramatically limits its ability to activate chlorine.

Laboratory measurements [Robinson et al. 1994, 1996] indicate that CF_2Cl_2 (CFC-12) is decomposed on alumina surfaces. Our model simulation with this process predicts an AAGTO *increase* of 4.2×10^{-5}% (scenario "H"). This ozone increase can be explained by the following. Alumina particles cause some loss of CF_2Cl_2 in the troposphere, which leads to slightly less CF_2Cl_2 reaching the stratosphere. Slightly less CF_2Cl_2 in the stratosphere results in the production of slightly less stratospheric Cl_y and, therefore, less ozone loss - which leads to a slight ozone increase.

4. Time-dependent Model Simulations and Results

Since the launch rate over the past 25 years has been generally smaller than our assumed launch rate of nine Space Shuttle and three Titan IV rockets per year, we also computed the time-dependent ozone changes resulting from a historical launch rate of the Space Shuttle, Titan III, and Titan IV vehicles. The launch rate for 1970-94 is taken from Isakowitz [1995] and for 1995-97 from R. Bennett [personal communication, 1998]. We ran four time-dependent model simulations for the period 1970-1997: 1) a "base" run which did not include any rocket launches; 2) an "alumina perturbed" run which included the historical launch rate with Al_2O_3 emissions only; 3) a "HCl perturbed" run which included the historical launch rate with HCl emissions only; and 4) a "total perturbed" run which included

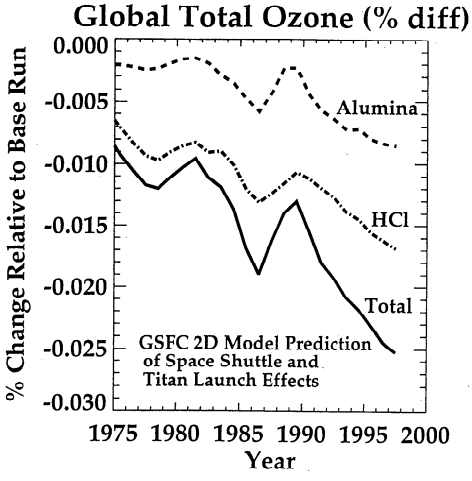

Figure 2. GSFC model calculated annually-averaged global total ozone change (percent) for the "alumina perturbed" run (dashed line), the "HCl perturbed" run (dash-dot line), and the "total perturbed" run (solid line) compared to the "base" run for the 1975-1997 time period. The "perturbed" runs include a historical launch rate of the Space Shuttle, Titan III, and Titan IV vehicles for the 1970-1997 period.

the historical launch rate with both HCl and Al_2O_3 emissions. The mass fraction of emitted alumina in the "alumina perturbed" and "total perturbed" runs was assumed to be 0.12, 0.08, and 0.80 in the small, medium, and large size distributions. The source gas boundary conditions for all four of these runs over this time period were taken from Table 6-3 of WMO [1995].

The AAGTO percentage difference of the "perturbed" runs compared to the "base" run is shown in Figure 2. Our model calculated ozone decrease shows variations over this time period. Local maximum ozone decreases are computed in years 1978, 1986, and 1997. The predicted variations in ozone decrease follow directly from the input rocket launch rates. The maximum AAGTO predicted decrease of 0.025% occurs in 1997 for the "total perturbed" compared to the "base" run.

The increasing influence of the emitted alumina in computed ozone loss is apparent over the 1975-1997 time period. The fractional contribution from the alumina to the total computed ozone loss caused by rocket launches increases from less than one-quarter to about one-third over this period. The background upper stratospheric amounts of inorganic chlorine increase over this period from about 1.5 to 3.5 ppbv, thus activation of the chlorine via the reaction $ClONO_2 + HCl \longrightarrow HNO_3 + Cl_2$ on the alumina particles becomes increasingly important.

Acknowledgments. The authors would like to express their gratitude to Robert R. Bennett (Thiokol Aerospace and Industrial Technologies) for his kind assistance in providing a listing of past space launches. The authors thank Marty N. Ross (The Aerospace Corporation), Michael J. Prather (University of California, Irvine), Mario J. Molina (Massachusetts Institute of Technology), and Malcolm K. W. Ko (AER, Inc.) for valuable discussions and comments regarding this study. We thank two reviewers for helpful suggestions regarding this manuscript. We also thank the NASA Atmospheric Chemistry Modeling and Analysis Program for its support.

References

Brady, B. B., and L. R. Martin, Modeling solid rocket booster exhaust plumes in the stratosphere with SURFACE CHEMKIN, Aerospace Report No. TR-95(5231)-9, September 1, 1995.

Brady, B. B., et al., Stratospheric ozone reactive chemicals generated by space launches worldwide, Aerospace Report No. TR-94(4231)-6, November 1, 1994.

Cofer, W. R., et al., Analysis of mid-tropospheric Space Shuttle exhausted aluminum oxide particles, *Atmos. Env., 21*, 1187-1196, 1987.

Cofer, W. R., et al., Space Shuttle exhausted aluminum oxide: a measured particle size distribution, *J. Geophys. Res., 96*, 17371-17376, 1991.

Danilin, M. Y., Local stratospheric effects of solid-fueled rocket emissions, *Ann. Geophysicae, 11*, 828-836, 1993.

Denison, M. R., et al., Solid rocket exhaust in the stratosphere: Plume diffusion and chemical reactions, *J. Spacecraft and Rockets, 31*, 435-442, 1994.

Isakowitz, S. J., International Reference Guide to Space Launch Systems, 2nd Edition, updated by Jeff Samella, published by AIAA, Washington, D.C., 1995.

Jackman, C. H., et al., Space Shuttle's impact on the stratosphere: an update, *J. Geophys. Res., 101*, 12523-12529, 1996a.

Jackman, C. H., et al., Past, present and future modeled ozone trends with comparisons to observed trends, *J. Geophys. Res., 101*, 28753-28767, 1996b.

Jones, A. E., et al., On the atmospheric impact of launching the Ariane 5 rocket, *J. Geophys. Res., 100*, 16651-16660, 1995.

Kasten, F., Falling speed of aerosol particles, *J. Appl. Met., 7*, 944-947, 1968.

Molina, M. J., et al., The reaction of $ClONO_2$ with HCl on aluminum oxide, *Geophys. Res. Lett., 24*, 1619-1622, 1997.

Prather, M. J., et al., The Space Shuttle's impact on the stratosphere, *J. Geophys. Res., 95*, 18583-18590, 1990.

Robinson, G. N., et al., Decomposition of halomethanes on α-alumina at stratospheric temperatures, *Geophys. Res. Lett., 21*, 377-380, 1994.

Robinson, G. N., et al., Correction to "decomposition of halomethanes on α-alumina at stratospheric temperatures," *Geophys. Res. Lett., 23*, 317, 1994.

Rogers, R. R., "A Short Course in Cloud Physics," Second Edition, New York, Pergamon Press, 1979.

Ross, M. N., et al., In-situ measurement of Cl_2 and O_3 in a stratospheric solid rocket motor exhaust plume, *Geophys. Res. Lett., 24*, 1755-1758, 1997a.

Ross, M. N., et al., Observation of stratospheric ozone depletion in rocket exhaust plumes, *Nature, 390*, 62-64, 1997b.

Strand, L. D., et al., Characterization of particulates in the exhaust plume of large solid- propellant rockets, *J. Spacecraft and Rockets, 18*, 297-305, 1981.

World Meteorological Organization (WMO), Scientific assessment of ozone depletion: 1994, *Rep. 37*, Global Ozone Res. and Monit. Proj., Geneva, 1995.

D. B. Considine, E. L. Fleming, C. H. Jackman, Atmospheric Chemistry and Dynamics Branch, Code 916, NASA/Goddard Space Flight Center, Greenbelt, MD 20771, (e-mail: jackman@assess.gsfc.nasa.gov).

(received October 8, 1997;
revised January 22, 1998;
accepted January 26, 1998.)